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UTILIZATION OF TECHNOGENIC PRODUCTS IN PRODUCTION OF CERAMIC BUILDING MATERIALS

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The possibility is studied and substantiated of using coal mining waste, metallurgical slag, oil shale processing products, and household waste in the production of ceramic construction materials. Practical recommendations are issued.

Ever expanding construction has resulted in the fact that the world construction industry (including that in Russia) has started experiencing a shortage of raw materials, especially of high-quality argillaceous material, which is the main component in the production of building ceramics.

Due to intense extraction, many argillaceous deposits are almost completely exhausted, and available resources in other deposits are rapidly being depleted.

The problem of sourcing high-quality argillaceous materials in Russia is especially pressing, since the rupture of economic ties that used to exist in the USSR, in particular, the ties with Ukraine, where the main deposits of high-quality materials are located, brought many ceramic factories to the brink of shutdown. In spite of the fact that in the last few years Ukraine has resumed supplying argillaceous minerals, their price has increased so significantly that manufacture of many types of ceramic products ceased to be profitable in the conditions of strong competition with the suppliers of similar products from Europe and Asia. The domestic producers are now often obliged to use clay from the Russian deposits, which are mostly located in Siberia and the Far East, which increases the cost of transportation to the site of production.

The above problems concern equally the traditional enterprises and the newly organized factories for structural wall ceramics (ceramic bricks and stones, roof tiles, tiles, etc.) in central Russia.

The known deposits of red-burning and light-burning clays in the European part of Russia are either exhausted or on the point of exhaustion. The situation calls for urgent survey and development of new deposits, which involve substantial financial costs, or a search for other radical ways which would be capable of solving or at least facilitating the solution of these problems.

One such way is the utilization of technogenic products for the purpose of complete or partial replacement of argillaceous minerals in the production of materials used in construction. Such technogenic products, which are now heaped in terraces occupying enormous areas of fertile land, include ash from coal-based power stations, coal mining wastes, some metallurgical slag, oil shale processing waste, and household waste.

A trend observed in the power industry in the last 20 – 25 years consists in the transition of many industrial sectors, including thermal power stations, from liquid and gas fuel to coal, which has produced an abrupt increase in the quantities of generated ash and slag. The amount of such waste in the end of the 1980s constituted around 500 mln tons per year, which was approximately equal to the volume of the world annual extraction of argillaceous minerals. To this quantity, one should add coal mining wastes, whose amount is approximately equal to that of ash or slightly higher, and oil shale processing waste, whose annual volume is nearly equal to the annual volume of clays extracted in Russia. Over decades, the technogenic products have been accumulated in industrial regions, taking space over vast territories of fertile lands and, under the effect of atmospheric factors, actively polluting the environment.

At present, over 1000 varieties of technogenic products in the world are considered promising for recycling. Out of that quantity, 780 products are included in various data banks; however, only 60 of them are recycled in practice [1].

The evaluation of the effect of various wastes on the environment is a labor-consuming and complicated process. Similar to other countries, Russia has evolved and approved

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TABLE 1

Coal field	Mass content in ash, %								
	SiO_2	Al_2O_3	TiO_2	Fe_2O_3	FeO	CaO	MgO	R_2O	calcination loss
Kuznetsk	51.6	23.7	0.8	2.6	2.3	2.1	1.3	1.5	14.2
Donetsk	52.1	22.3	0.7	2.1	1.3	1.6	1.1	1.8	16.6
Moskovian	48.2	33.1	0.7	2.5	1.8	1.1	0.9	2.5	11.1

maximum permissible concentrations (MPC) for nearly 600 types of agents and compounds, although the number of agents and compounds used in various production sectors counts tens of thousands. Considering that the development of a MPC standard for a single compound takes 2 – 3 years [2], one can perceive the difficulties encountered by the researchers in this field. It should be noted that MPC values are developed based on the average statistical sanitary norms in coordination with various agencies, which often try unjustifiably to increase the MPC values [3].

An erroneous approach to the problem of accumulation and utilization of various wastes resulted in the fact that the environmental-protection industry in the FSU states was insufficiently developed and incapable of solving the problems it was meant to solve. Thus, only one waste-processing factory employing 120 persons is currently functioning in Russia, whereas in the USA, over 1 million people are engaged in this sector of industry.

The calculations show that integrated utilization of raw materials and technogenic products would make it possible to increase the production of many types of articles by 25 – 30%. Taking into account the reduced costs of geological surveys, extraction and storage of raw materials, land recultivation, and environment-related activities, the recycled production cost would be lower by the factor of 2 – 4 than using raw materials extracted according to traditional technologies [4]. The economic effect of recycling of technogenic products is largely determined by the fact that they can be used in production without a need to extract raw materials. In the case when the technogenic products are recycled in the same place where they are generated, that is, in industrially developed regions, which have a high demand for building materials, the transportation costs are minimal.

The main types of technogenic products in Russia are power plant ashes, coal mining wastes, mining-and-concentration works waste, oil shale processing waste, and household waste.

Household waste in our country is virtually not utilized, since there is up to now a lack of efficient technological solutions to this problem. Metallurgical waste in the form of granulated slag is almost completely utilized in the production of binding agents [5].

The industrial experience of using waste from the Kachkanarskii Mining-and-Concentration Works in the production of ceramic tiles at Kuchinskii Ceramic Factory demonstrated that these technogenic materials (especially those containing minerals of the pyroxene class) can be utilized without substantial expense in the production of ceramic building materials [6]. The total volume of waste generated by mining-and-concentration works in Russia reaches 50 million tons per year, whereas the amount of utilized materials does not exceed several thousands tons.

The coal mining waste and the entrainment ash generated by power plants, with respect to their mineralogical composition and the accumulated quantities, are most promising as auxiliary or main materials in the production of building materials, including ceramics.

The technogenic materials of this group belong to large-scale wastes: the amount of coal concentration waste reaches 90 mln tons per year, and that of slag-ash waste from power plants is about 100 mln tons per year [7].

Unfortunately, Russia at present does not have an integrated program for the utilization of fuel-containing mineral wastes in the construction industry, like the “Raw Materials” program that used to exist in the USSR. Today, only around 1% of the annually generated technogenic waste of this type is recycled in such a way. However, the experience of industrial use of such technogenic products in the recent past demonstrated that these products can serve not only as correcting and auxiliary additives, but also can be used as the main mineral material in production of building ceramics.

The similarity of the chemico-mineralogical composition of the entrainment ash generated by power plants and the composition of natural argillaceous minerals (Table 1) makes is possible to consider such ash as an inexhaustible source of high-quality argillaceous material.

In using coal from a particular coal field, the entrainment ash from power plants has a sufficiently stable chemical composition, which makes it possible to predict the quality of the building material produced on the basis of such ash. After coal combustion, solid conglomerates of different compounds are formed, which in the form of a dust fraction with the specific surface area of 1500 – 3500 cm^2/g are entrained with the flue gases (over 90%), and larger conglomerates settle on the furnace bottom in the form of melted lump slag [7].

The inorganic part of entrainment ash is a combination of various vitreous and crystalline components, mainly, metakaolinite, mullite, and free quartz; calcium silicates and aluminosilicates are present as well. Depending on the chemical composition, the ash sinters at temperatures below 1350°C, i.e., according to the argillaceous classification, it belongs to low-melting minerals.

The physicochemical basis of ceramic production based on argillaceous materials (including entrainment ash and coal mining waste) is the synthesis of primary mullite in firing, which determines the main physicomechanical properties of the end product. Since ash already contains some mullite, in the course of ceramic crock formation under firing, second-

ary mullite and, with a high degree of probability, anorthite will be synthesized from ash metakaolinite.

It is known that entrainment ash, which consists of fused particles of spherulite structure, in spite of its rather high dispersion, weakly reacts with the argillaceous mineral components under firing and in fact acts as the grog component in clay mixtures.

It was experimentally proved that ash is least active immediately after moisture removal; therefore, in order to enhance its reaction capacity, several conditions ought to be fulfilled:

– ash from dump heaps should be used after aging in natural conditions for a long period (over one year);

– the spherulite structure of ash should be destroyed by milling.

Starting with the 1980s, the Moscow Institute of Municipal Economics and Construction has been carrying out systematic studies of the utilization of the entrainment ash from Luberetskii Power Plant in mixtures for ceramic material production. Clays from virtually all known deposits in Russia, including the recently developed ones (Mikhnevskoe, Vladimirskoe, Shchelkovskoe, Egor’evskoe, Kurganskoe, etc.), were used as the main material component in these mixtures.

The best results were obtained in using clays of moderate and high plasticity (plasticity number over 15). Thus, the use of light-burning clays from the Lukoshkinskoe high-melting clay quarry (Lipetsk region), whose plasticity number is over 20, made it possible to introduce into the mixture up to 25% entrainment ash generated by the Luberetskii Power Plant from long-storage terraces, without preliminary treatment of the ash.

The industrially produced ceramic bricks based on this mixture fully satisfied the requirements of GOST 7484–78. The brick grade was M350, the cold resistance 35 cycles, and the porosity correlated with the “effective ceramics” category.

Even better results were obtained after slip preparation of the mixture, including subsequent drying of the slip to obtain a plastic mixture of 18% moisture and a molding powder of 6 – 8% moisture. The batch was prepared from experimental mixtures with the ash content ranging from 15 to 50% (here and elsewhere mass content is indicated), using the method of separate or combined mixture preparation.

In the case of separate preparation of the mixture, clay was liquefied in a laboratory mixer until getting a slip of 50% moisture. Ash was milled in a laboratory drum mill by wet grinding, employing metal balls in the ratio material : water : balls equal to 1 : 0.75 : 2, for 1, 3, and 5 h. The resulting slips were mixed inside the laboratory mixer in a specified ratio and dried in a lab drying cabinet to moisture levels of 18 and 8%. After the plastic mixture with 18% moisture aged in a sealed container, it was used for plastic molding of samples, which were dried to a moisture content of not more than 2% and fired in the laboratory kiln at temperatures of 900, 950, and 1000°C.

The studies of the experimental samples indicated that the physicomechanical properties of the products depend on the following factors:

– the chemical and mineralogical composition of the clay used;

– the ratio between the clay and the entrainment ash;

– the ash milling duration;

– the firing temperature of the experimental samples.

An increase in the dispersion and plasticity of clay results in a gradual increase in the physicomechanical properties of experimental samples. An increase in the ash content in the batch from 15 to 50% produces a gradual decrease in the mechanical strength of the samples and increased porosity. However, the compressive strength of the samples containing up to 50% ash remains sufficiently high (over 30 MPa). An increase in the ash milling duration makes it possible to produce articles with higher mechanical strength, even with the maximum ash content.

With the firing temperature over 900°C and the ash content over 25%, most of the experimental samples had swelled; however, with a firing temperature of 900°C and an ash content up to 50%, no deformation was registered in the samples. At the same time, the linear fire shrinkage did not exceed 2%, the water absorption varied from 5 to 12%, depending on the quantity of ash in the batch, and the mechanical strength ranged from 15 to 250 MPa.

Analysis of the obtained data suggests that the reaction capacity of the entrainment ash subjected to an effective mechanical treatment grows to such an extent that its starts actively reacting with argillaceous minerals. At the same time, the entrainment ash in drying behaves in the same way as dehydrated clay, and in firing passes via the same stages as argillaceous minerals: decomposition of carbonates, formation of mullite, etc. [8]. Furthermore, the entrainment ash under firing acts as a rather active flux, which in some cases makes it possible to decrease the sintering temperature by 50 – 100°C. This is especially true of light-burning high-melting and refractory clays (Lukoshkinskoe, Latnenskoe, and other deposits), in using which the introduction of ash to the batch enables one to decrease the sintering temperature from 1100 to 900 – 930°C.

It should be noted as well that the prototype lot of facade tiles produced on the production line of the Kuchinskii Ceramic Factory from molding powder (moisture 6%), which contained 80% clay and 20% ash, fully met the requirements of GOST 13996.

Even better results were obtained in the combined mixture preparation. The clay and ash were mixed in a prescribed ratio and milled in a laboratory ball mill, employing metal balls with a batch : water : balls ratio equal to 1 : 1 : 2, for 1, 3, and 5 h. The slip prepared in such way was dried to obtain a molding mixture of 18% moisture and a molding powder of moisture 8%. The molding mixture was used for plastic molding of samples, which were then treated according to the above-described technological scheme.

The physicomechanical properties of the experimental samples fired at 900°C with exposure at this temperature for 1 h significantly exceeded the properties of similar samples made of the mixture produced by the separate preparation method: their water absorption was 5 – 7%, and mechanical strength was up to 50 MPa.

The molding powder produced by drying the slip to 8% moisture was first crushed in the laboratory roll, then sifted through a sieve with the cell size 2 mm, held in a sealed container for 24 h, and then used to mold experimental samples at a specific pressure of 20, 30, and 40 MPa.

After drying to a moisture content of not more than 2%, the samples were fired in the laboratory kiln at 900°C for 1 h. The visual inspection of the samples after firing showed that 1 h exposure was insufficient for samples with an ash content over 25%, as the sample core was black. To prevent this phenomenon, the exposure duration was extended to 2 h, after which the black core disappeared. On the whole, the investigation results testify to very good physicomechanical parameters of the samples: shrinkage 0.75 – 2%, water absorption below 5%, compressive strength up to 100 MPa.

Analysis of the experimental samples suggests the following conclusions:

– power plant entrainment ash after respective treatment is a promising material for ceramic production;

– combined mixture preparation provides for articles with very good physicomechanical parameters, even with a high ash content in the batch;

– the introduction of ash to the batch makes it possible to decrease the temperature of firing ceramic articles by 50 – 100°C;

– the use of ash in mixtures for coarse construction ceramics makes it possible to improve the color of produced articles (to a pale-cream shade), even when using red-burning clay as the main material.

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